

Report Entitled:

**Electrochemical Characterization of BlackLight Power, Inc. MH
as Electrodes for Li-ion Batteries**

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Electrochemical Characterization of BlackLight Power, Inc MH as Electrode for Li-ion Batteries

Experimental:

The following materials were tested as received from BlackLight Inc: (i) SrH_xBr_y , (ii) CaH_xBr_y , (iii) CaH_xCl_y , (iv) KH_xBr_y (v) KH_xI_y . Electrochemical characterization of the above materials as electrode for Li-ion battery system was carried out in Swagelok three electrode cells (T cells) presented in Fig. 1A. The anode and the reference electrodes were discs of lithium foil, and the separator was a sheet of Whatman glass fiber filter paper. The cathode consisted of a mixture of the BL/MH, carbon black and poly(tetrafluoroethylene) which was pressed into a thin film 50-60 μm thick. The electrolyte used was 1 M LiPF_6 in a 1:1:3 mixture of propylene carbonate, ethylene carbonate and dimethyl carbonate (EM Industries).¹⁻⁴ Handling of materials and cell assembling was carried out in an Ar-filled glove box with water content less than 5 ppm (Vaccum Atmospheres).

The rest potential of all tested materials was 3.1 V vs. Li/Li^+ reference electrode. To fingerprint the potentials at which the redox reactions occur and to determine their electrochemical reversibility, the cyclic voltammograms were obtained for all materials at potential range from their rest potential in the cathodic direction to 0.5 V vs. Li/Li^+ . Next, the potential was reversed in the anodic direction to 3.5V and 4.2 V vs. Li/Li^+ reference electrode. The scan rate was 0.1 mV/s for all cases.

Results and Discussion:

Fig. 1 presents cyclic voltammograms obtained for sample A (KH_xI_y 990630 MWNA). The cathode was cycled between 0.5 V and 4.2 V vs Li/Li^+ reference electrode using a scan rate of 0.1 mV/s. As shown in Fig. 1 a small peak with a peak current less than 0.07 A/g is observed at 1.95 V vs Li/Li^+ reference electrode indicating reduction of the electrode active material. Anodically, there is a current plateau of 0.002 A/g from 1.6 V up to 3.95 V when a large increase of the current was observed. At this potential gassing of the electrode occurred, indicating that the observed current may be due to the irreversible oxidation of the active material through a gas

evolution reaction. As shown in Fig. 1, after the scanned potential passes through 4.2 V and returns in a negative direction, larger currents are observed at less positive potentials due to the parasitic gas reaction. In the second cycle almost identical redox behavior was observed. To understand better the processes occurring at 4.2V, an attempt was made to charge the cathode under constant current (CC) mode until the electrode potential reaches 4.2 V and by keeping the electrode potential constant at 4.2 V, the material was charged under constant voltage mode (CV). The objective of this study was: (i) to determine the amount of charge/g necessary for a complete charge of the material (CC mode) and (ii) to determine the presence of any diffusion of the electroactive species (H) in bulk of the active material (CV mode). To test the cells, charge - discharge studies were done using currents of $50 \mu\text{A}$.

Under the CC mode, it took only several seconds with a total charge of 4 to 5 mA/g to charge the electrode to 4.2 V vs Li/Li^+ reference electrode. However, when the polarization was stopped, the potential dropped immediately from 4.2 V to its open circuit potential value of 3.1V indicating that the material cannot be charged above 3.2 V. Thus, the open circuit potential observed initially at 3.2 V was actually a potential at which the materials was in its oxidized form.

The CV data obtained analyzing the sample A (KH_xI_y , 990630 mwnA) in the region between 0.5 V and 3.2 V vs Li/Li^+ reference electrode indicated that the cathode material is not reversible over the entire intercalation range. Anodic peak was not observed when the electrode was cycled in the positive direction indicating that the active material cannot be oxidized back reversibly to its initial oxidation state.

Fig. 2 presents cyclic voltammograms obtained for the sample B (CaH_xCl_y , 990723 mwnA). The voltage was varied between 0.5 V and 4.2 V (Fig. 2B) and between 0.5 V and 3.0 V vs Li/Li^+ reference electrode. The scan between 0.5 V and 3.0 V was used to avoid any possible structural breakdown of the active material at high overpotentials (4.2 V).

Fig. 2 B shows a very well developed cathodic peak at 2.0 V vs Li/Li^+ reference electrode with a very high peak current of 45 mA/g. The anodic peak observed in the reverse scan, Fig. 2A was smaller 10 mA/g. However, this material shows better reversibility than A (KH_xI_y , 990630 mwnA). The initial studies indicated that B (CaH_xCl_y , 990723 mwnA) may be used to construct a primary battery. To utilize this material as a cathode material for secondary batteries, further studies will be necessary with an objective to improve its electrochemical reversibility.

Fig. 3 presents cyclic voltammograms obtained for the sample C(CaH_xBr_y 990812mwnA). The voltage was varied between 0.5 V and 4.2 V vs Li/Li^+ reference electrode using a scan rate of 0.1 mV/sec.

Sample C(CaH_xBr_y 990812mwnA) exhibits almost the same electrochemical characteristics as sample B(CaH_xCl_y 990723 mwnA). As shown in Fig.3 a very well developed cathodic peak is observed at 2.0 V vs Li/Li^+ reference electrode with a very high peak current of approximately 50 mA/g. The anodic peak was absent in the reverse scan, until the electrode reaches an anodic potential of 3.2 V. The nature of the current observed at potentials higher than 3.2 V was discussed in details in Fig. 1.

The initial studies indicated that the material B(CaH_xCl_y 990723 mwnA) can be used to construct a primary battery. To utilize this material as a cathode material for secondary batteries, further studies should have an objective to improve its electrochemical reversibility.

Fig. 4 presents cyclic voltammograms obtained for the sample D(CaH_xBr_y 990819mwnA). The voltage was varied between 0.5 V and 3.6 V vs Li/Li^+ reference electrode using a scan rate of 0.1 mV/sec. The electrode was scanned to only 3.6 V to avoid any possible structural breakdown of the active material at higher overpotentials.

Sample D(CaH_xBr_y 990819mwnA) exhibits similar electrochemical characteristics when compared with the other samples. As shown in Fig.4, the cathodic peak is shifted in cathodic direction (1.2 V vs Li/Li^+ reference electrode). Two anodic peaks are observed in the positive direction. One is almost reversible to the cathodic peak at 1.2 V and the other was observed at 1.8 V. The peak current (5 mA/g) observed in the first cycle is almost 10 times smaller than in the case of sample C. In the second cycle the peak current decreases to a value of 2mA/g and then in the third and the fourth cycle stabilizes to a value of 1.5 mA/g.

Both anodic peaks are stable with anodic peak current of 1mA/g. Further studies should have an objective to increase (i) the electrochemical reversibility and (ii) capacity of this material.

Fig. 5 presents cyclic voltammograms obtained for the sample E(SrH_xBr_y 990812mwnA). The voltage was varied between 0.5 V and 4.2 V vs Li/Li^+ reference electrode using a scan rate of 0.1 mV/sec. This sample was not stable in the electrolyte. Several T cells were constructed in a glove box using this material. However, it was not possible to obtain any current response from

the electrode/electrolyte (1 M LiPF_6 in a 1:1:3 mixture of propylene carbonate, ethylene carbonate and dimethyl carbonate) interface.

Figures 6 and 7 show the charge-discharge curves obtained for samples A and D, respectively. Similar results were obtained for the other samples. The electrode was cycled between 0.5 and 4.2 V at the rate of 50 μA . All materials showed low reversible capacity of approximately 5 mA/g. To use these materials as cathodes in Li-ion secondary batteries it will necessary to improve the stability in the electrolyte and their reversible capacity.

The samples A, B and C show large initial irreversible capacity which can be use to power primary Li batteries.

References

1. P. Yu, B. N. Popov, J. A. Ritter and R. E. White, "Determination of the Lithium Ion Diffusion Coefficient in Graphite," *J. Electrochem. Soc.*, **146**, (1), 8-14 (1999).
2. Dong Zhang, Branko Popov, Pankaj Arora and Ralph E. White, "Cobalt Doped Chromium Oxides as Cathode Materials for Secondary Batteries," *J. of Power Sources*, **83**, 121 (1999).
3. B. N. Popov, Battery Work at University of South Carolina, *Automotive Technology Development*, **1**, 371-397 (1997) DOE, Energy Efficiency and Renewable Energy, Office of Transportation Technologies, Washington, DC. (1997).
4. P. Arora, B. N. Popov and R. E. White, Electrochemical Investigation of Cobalt-Doped LiMn_2O_4 as Cathode Material for Li-ion Batteries. *J. Electrochem. Soc.* **145**, 807 (1998).

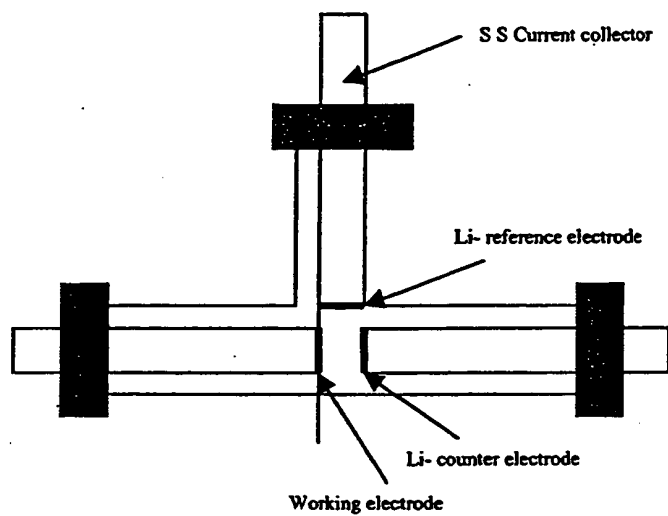


Fig. 1A Schematic of Swagelok type three electrode cell (T - cell)

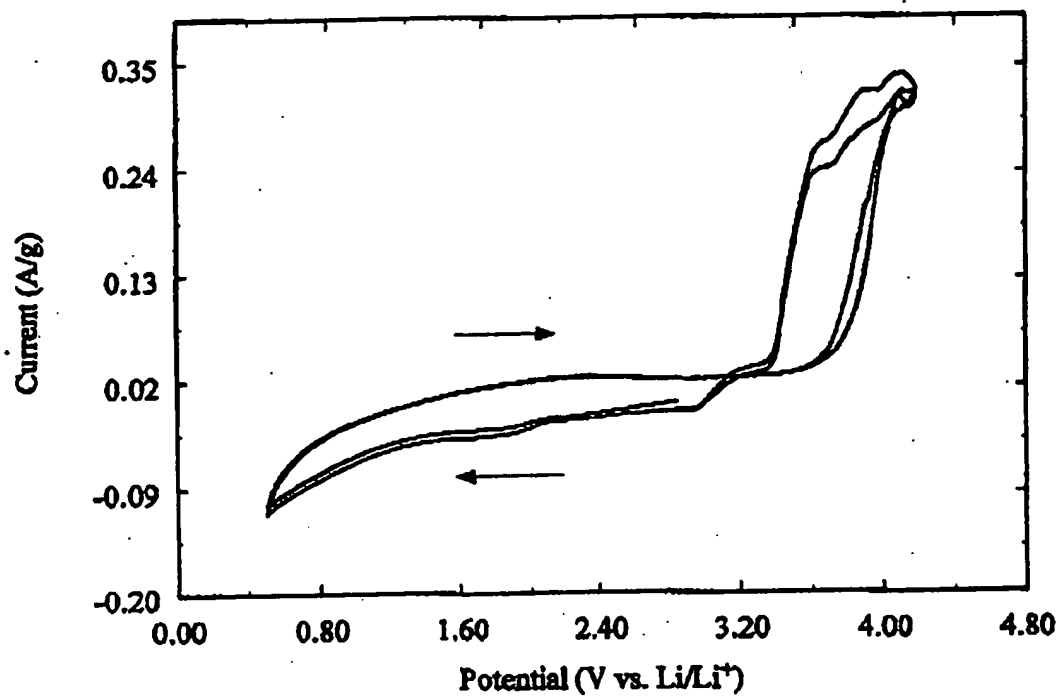


Figure 1

Cyclic voltammograms of sample A
Weight of Cathode - 30 mg
Scan Rate - 0.1 mV/sec
Potential window - 0.5 V to 4.2 V

Index

A - 990630MWNA
B - 990723MWNE
C - 990812MWNA
D - 990819MWNA
E - 990812MWNC

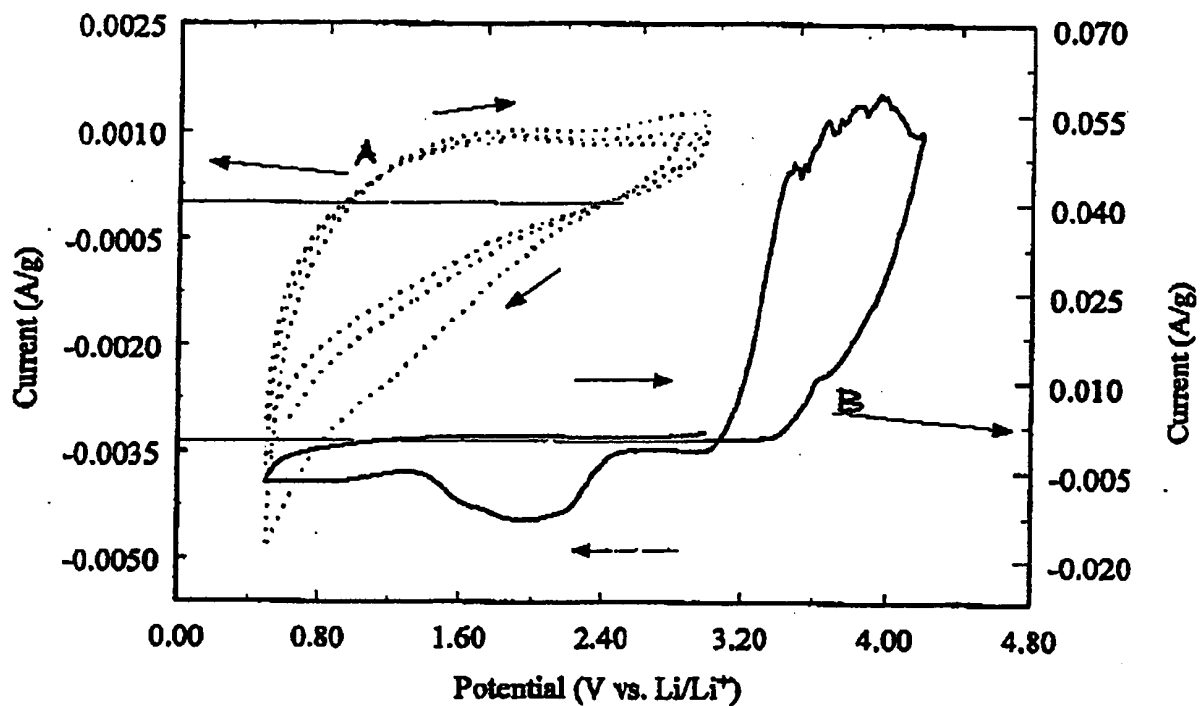


Figure 2

Cyclic voltammogram of sample B

Weight of Cathode - 30 mg

Scan Rate - 0.1 mV/sec

Potential window

(A) - 3.0 V - 0.5 V

(B) - 4.2 V - 0.5 V

Index

A - 990630MWNA

B - 990723MWNE

C - 990812MWNA

D - 990819MWNA

E - 990812MWNC

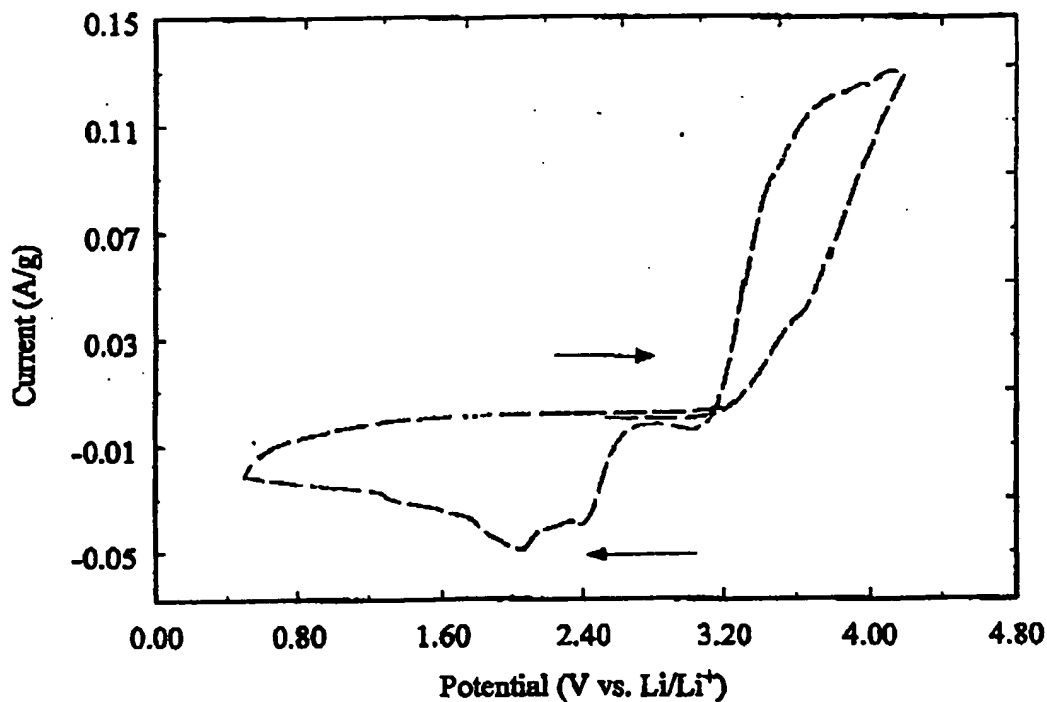


Figure 3

Cyclic voltammogram of sample C

Weight of Cathode - 30 mg

Scan Rate - 0.1 mV/sec

Potential window - 4.2 V - 0.5 V

Index

A - 990630MWNA

B - 990723MWNE

C - 990812MWNA

D - 990819MWNA

E - 990812MWNC

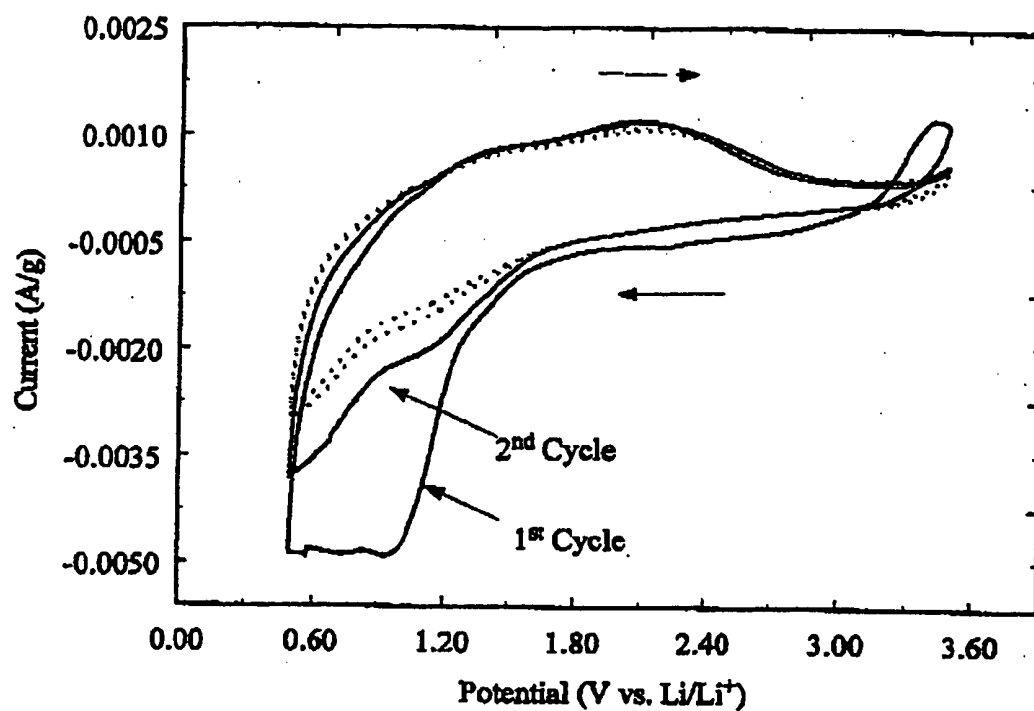


Figure 4

Cyclic voltammograms of sample D

Weight of Cathode - 30 mg

Scan Rate - 0.1 mV/sec

Potential window - 4.2 V - 0.5 V

Index

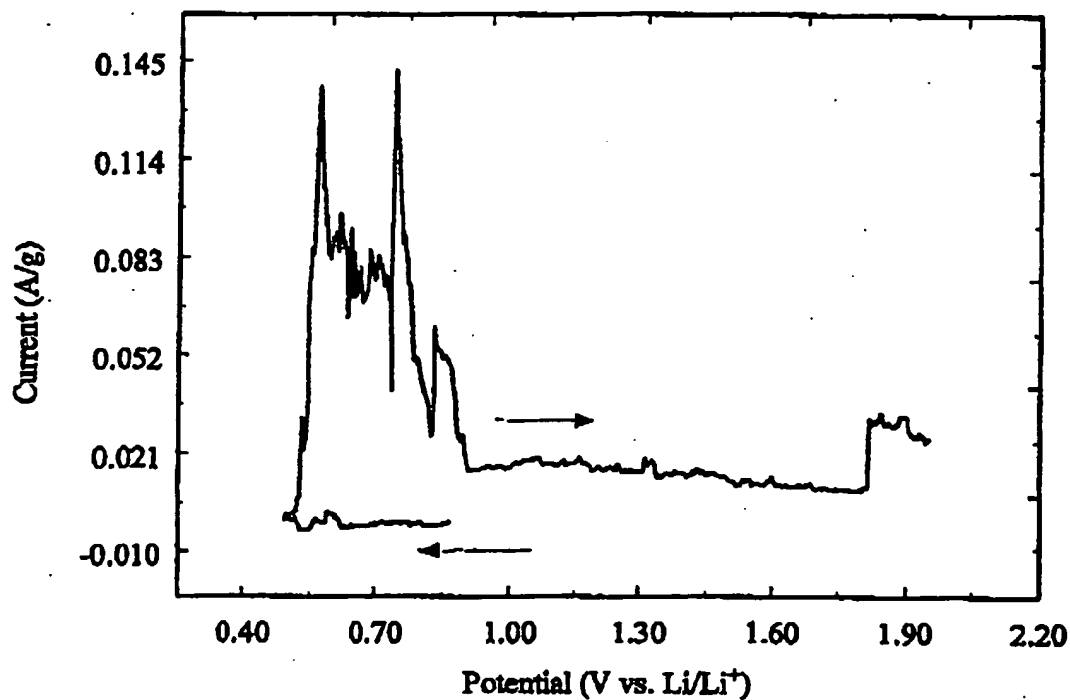
A - 990630MWNA

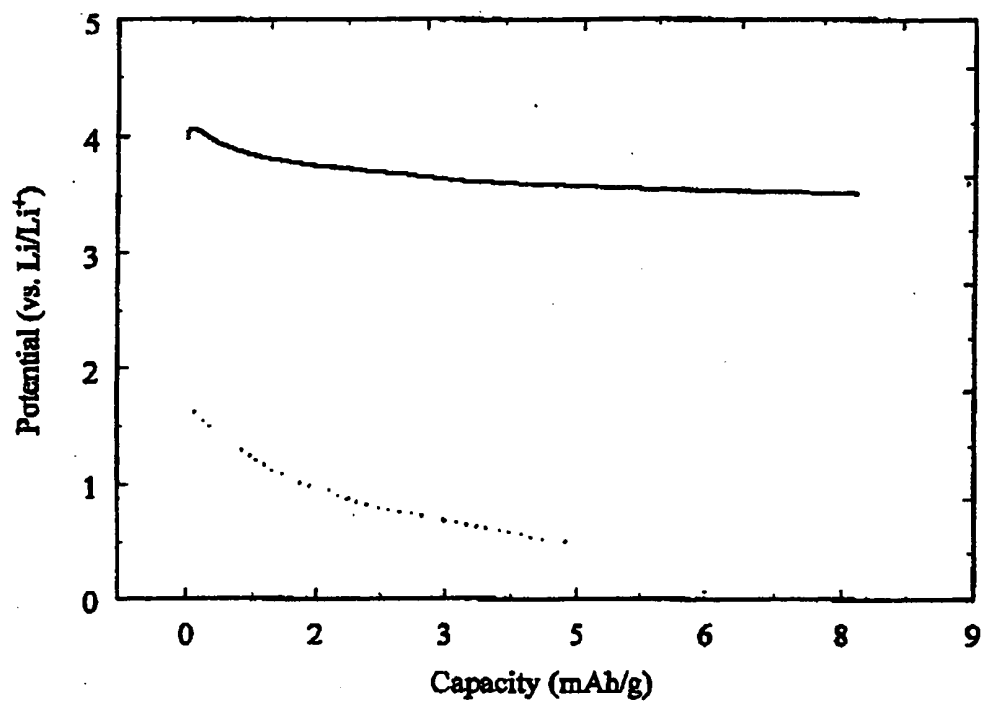
B - 990723MWNE

C - 990812MWNA

D - 990819MWNA

E - 990812MWNC

**Figure 5****Cyclic Voltammogram of Sample E****Reference/Counter Electrode - Li****Weight of active material - 30 mg (10% binder)****Scan Rate - 0.1 mV/sec****Potential window - 4.2 V - 0.5 V****Index****A - 990630MWNA****B - 990723MWNE****C - 990812MWNA****D - 990819MWNA****E - 990812MWNC**

**Figure 6**

Charge Discharge characteristics of sample A

Weight of Cathode - 30 mg

Charge - Discharge current - 50 μ A

Index

A - 990630MWNA

B - 990723MWNE

C - 990812MWNA

D - 990819MWNA

E - 990812MWNC

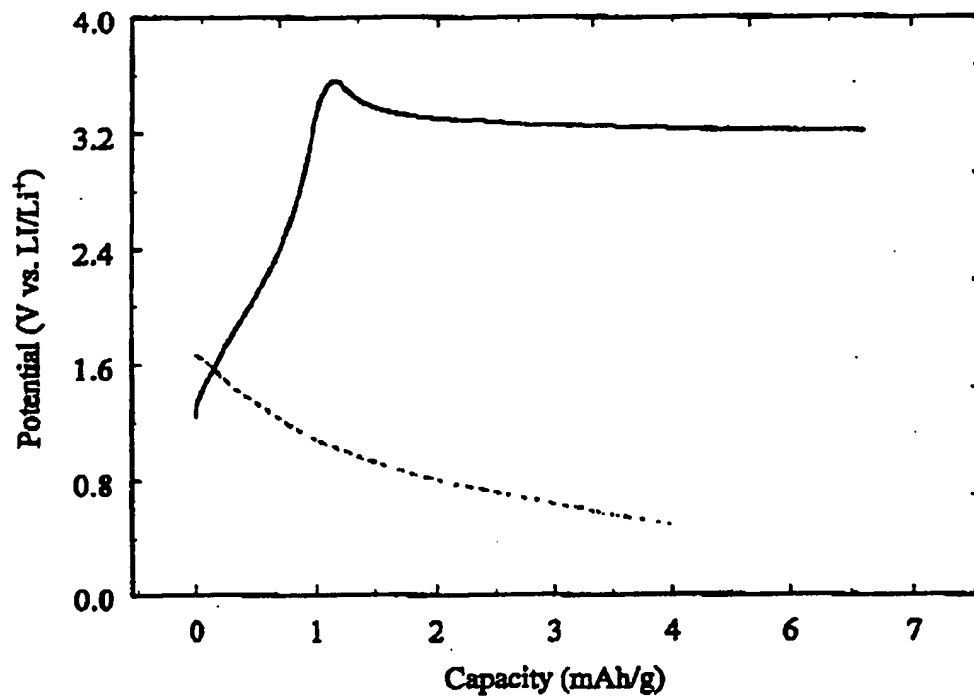


Figure 7

Charge Discharge characteristics of sample D

Weight of Cathode - 30 mg

Charge - Discharge current - 50 μ A

Index

A - 990630MWNA

B - 990723MWNE

C - 990812MWNA

D - 990819MWNA

E - 990812MWNC

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